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10-Vertex *closo*-carborane: a unique ligand platform for porous coordination polymers†

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1,10-Dicarboxy-1,10-dicarba-*closo*-decaborane, a classical dicarboxylate spacer ligand type similar to the prototypical terephthalic acid, proved to be different not only from the latter, but also from its closest relative compound, 1,12-dicarboxy-*closo*-1,12-dicarbadecaborane, with regard to the topology of its derived PCPs. Highly porous and robust compounds of zinc (**rob** net) and cobalt ('quasi' **pcu**) as well as a topologically unexpected copper compound (**lvt**) define the individuality of the 10-vertex carborane cage as a new fundamental spacer type in PCP chemistry. A combination of a lower steric demand compared to the 12-vertex analogue, a preferred orientation angle of 45° between the carboxylate planes and a moderately low rotation barrier are held responsible for the uniqueness of the 10-vertex analogue.

Porous Coordination Polymers (PCPs), also known as Metal Organic Frameworks (MOFs), constitute an established area of research[1] with a high variety of objects and with a focus recently shifting to their potential use in applications such as gas adsorption and separation, catalysis and drug delivery, to list the most important ones.[2] The surface area of these materials could exceed 6000 $m^2\ g^{-1}$, which is already close to the theoretical maximum of 1–1.5 $10^4\ m^2\ g^{-1}$.[3] The best PCPs in terms of stability and accessible surface areas (*e.g.* the well-known MIL-101, UiO-66, ZIF-8, MFU-1,2 and IRMOF analogues) are mostly built from simple symmetric building blocks and coordination bonding clusters. The latter play very straightforward connector/node roles, and the resulting frameworks represent simple periodic nets in accordance with Robson's seminal vision.[4] The extremely high surface areas of the best PCPs are achieved when the framework's topology corresponds to a simple periodic net with high symmetry. According to a topological view, there should be no difference between linear ligands of different types.

Whether the latter statement is true is context dependent. On the one hand, the classic IRMOF series[5] proves the equivalence of linear building blocks, notwithstanding their relative size. On the other hand, even slight substitution of building blocks might spoil self-assembly schemes. Broad isomerism does exist, influenced even by weak factors, such as minor steric effects or intermolecular-interaction influences, *i.e.* by the nature of the functionalized molecular platform. The affinity towards guest molecules, and hence the whole plethora of properties important for applications, depends on the nature of building blocks. The ultimate approach would be additional functional utilization of a linker's core, typically considered as an inert supporting strut, which constitutes, however, a significant, often major, part of a framework in terms of weight.[6]

However, the number of fundamentally different molecular platforms suitable to support simple linear building blocks is relatively small. Aside from acetylene and benzene, prototypical cage compounds, namely bicyclo[2.2.2]octane and cubane (some highly reactive propellanes are not truly viable) should be named. This prototypical set translates to a number of derivatives containing heterocyclic or unsaturated fragments, as well as homologation or annealing of the single blocks or their combinations.[7]

This list, which represents a rather organic viewpoint, is not complete because some non-classical, more inorganic platforms, whose potential, according to our anticipations, is still to be disclosed in the PCP area. Robust *closo*-carboranes

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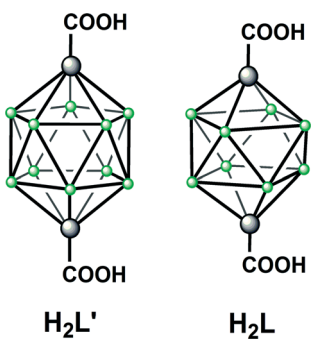
represent an interesting class of 3D σ-aromatic cages,[8] which is the focus of our current interest. Boron is a light element, which assures high specific surface areas of its derived materials, which exhibit different surface properties defined by the hydridic character of the protons at the BH 'vertices', compared to the usual CH-defined ones, potentially providing special sorption possibilities.

The interest in carboranes is obvious[9] and some initial efforts were directed towards the exploration of some zinc,[10] cobalt,[11] and very recently, lanthanide[12] PCPs based on 1,12-dicarboxy-1,12-dicarba-*closo*-dodecaborane, H_2L' (Scheme 1). All the previously reported compounds with dominantly 12-vertex carborane-based spacers have relatively low experimentally proven surface areas (rarely exceeding 300 $m^2\ g^{-1}$), but demonstrate some promising properties, like good adsorption selectivities of CO_2 achieved typically because of very narrow slit pores. In general, the porosity of the carborane-based PCPs did not match the expectations based on a comparison with analogous terephthalate PCPs. The efforts to prepare highly porous carborane-based PCPs are not languishing, with the NU-135 copper PCP being a successful achievement;[13] however, the carborane share in the linker amounts to only ~1/3 and the structure is equivalent to the prototypical NOTT-101 PCP based on triphenylene building block.[14]

Stimulated by the strangely elusive goal of synthesizing a MOF-5 analogue using 1,12-dicarboxy-1,12-dicarba-*closo*-dodecaborane, or at least to produce predominantly carborane-based PCPs with significant porosity, we turned a smaller, 10-vertex based analogue, 1,10-dicarboxy-1,10-dicarba-*closo*-dodecaborane (H_2L) (Scheme 1),[15] conjecturing that even slight steric truncation could be of crucial importance during self-assembly. Further, the slightly higher strain of the bicapped square-antiprismatic form of the 10-vertex carborane compared to that of the icosahedral 12-vertex carborane could tune physisorption, an effect worthy to be measured experimentally. It is also worth noting that the derivatives of the 10-vertex *closo-p*-carborane are also characterized by high thermal stability,[16] practically rather limited by decarboxylative degradation.

In this contribution, we report zinc, cobalt and copper PCPs of the new carborane ligand, L^{2-}, used for the first time in the role of a building block for PCPs. We demonstrate the notable peculiarities of the resulting materials in terms of their topology, porosity and physisorption (or rather one of the first due to the advent of a very recent example of the NU-700 PCP, $[Cu_3L]_2$, based on the tritopic H_3L = 1,3,5-tris-(10-carboxy-1,10-dicarba-*closo*-1,10-decaboran-yl)benzene ligand).[17]



Scheme 1

All the PCP compounds were synthesized by variation of standard low temperature solvothermal crystallization in amide (typically DMF)-based solvent mixtures (see the ESI†). In the case of zinc, a transient phase (needle crystals) was observed as the first product, but it is converted mostly to another phase (blocks) within ~12 h at 80 °C in a 1:1 DEF/EtOH solution (DEF = *N*,*N*-diethylformamide).

Although intrigued by the idea of supramolecular isomerism, we focused on the investigation of the final stable phase, which could be easily obtained in pure form. SC XRD structure determination revealed that $[Zn_4OL_3(DEF)_3]$ (**1**) is based on the targeted $\{Zn_4O(COO)_6\}$ secondary building unit (SBU)[5] (Fig. 1).

All previous attempts to synthesize a MOF-5 structure with dicarba-*closo*-dodecacarborane-based ligands yielded structures based on clusters with additional oxy/oxo ligands involved, like $[Zn_3(OH)(L')_{2.5}(DEF)_4]_n$ (with a Brunauer–Emmett–Teller surface area of S_{BET} = 250 $m^2\ g^{-1}$).[10] The reason for such a difference could be the slightly lower steric demand of

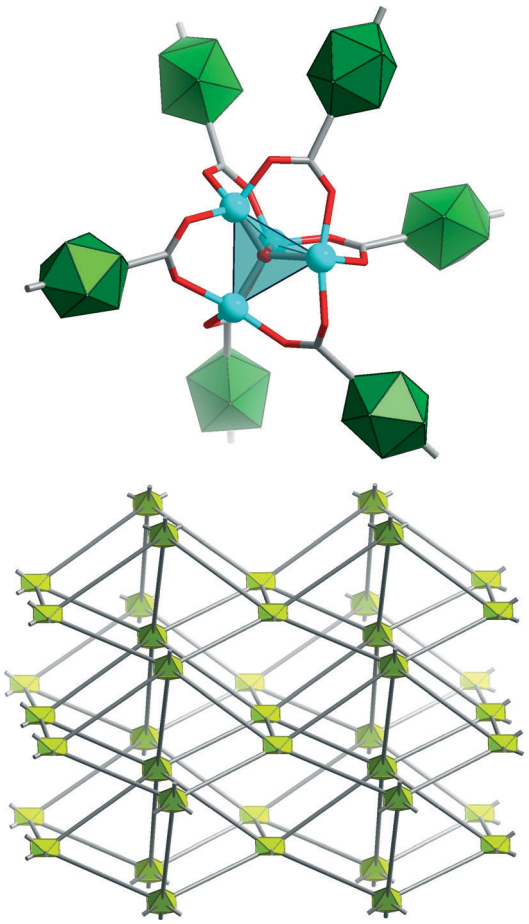


Fig. 1 Structure of **1** based on a characteristic, albeit deformed (see the asterisk), $\{Zn_4O(RCO_2)_6\}$ synthon (top), and the topological representation of the resultant **lvt** net (bottom).

the ligand based on the 10-vertex carborane, but the concomitant polymorphism observed for this case suggests that the synthesis of a 12-vertex analogue is not impossible. Surprisingly, although the characteristic SBU is realized, one of the 'links' deflects significantly from the direction defined by the highest symmetry and the resultant 6-connected framework does not have a **pcu**, but an **lvt** net topology (Table 1). In spite of the slightly smaller pore opening size (~4 × 4 Å vdW for **1**, Fig. S6†), the void volume and the surface area are conditioned to be close to those of the **pcu**-isomer. The activated **1a**, prepared by direct degassing (unlike other low porosity 12-vertex carborane-based analogs), shows a significant surface area of S_{BET} = 896 m^2 g^{-1} (N_2, 77 K) (Fig. 3), which could probably be improved towards the anticipated maximum of ~1945 m^2 g^{-1} (calculated value based on structural data)[18] by application of milder degassing methods. The difference is not unique for zinc MOFs, including MOF-5, with the contributing factors not only interpenetration, but more generally, partial pore obturation caused by hydrolytic degradation.[19]

Analogous crystallization conditions using cobalt nitrate and DMF yielded [Co(DMF)L] (**2**) as a product. In the crystal structure, the two crystallographically distinct, but chemically and topologically equivalent cobalt atoms have regular octahedral environments consisting of four equatorial oxygen atoms of bridging carboxylates and two bridging axial oxygen atoms of *N*,*N*-dimethylformamide's carbonyl group. The cobalt atoms are associated in a chain of corner sharing octahedra, with additional connections ensured by bridging carboxylate groups, which are equivalent to 'face-to-face' connections (Fig. 2, top). The chains of the opposing face connected octahedra are interconnected by means of bifunctional ligands, that is, by the carborane struts (Fig. 2, bottom). As the coordination bonded clusters are infinite, the topological analysis needs arbitrary dissection to finite subunits. A minimal, purely translational repeating unit in terms of connectivity consists of two cobalt atoms, and this unit could be formally considered as a 6-connected node of a primitive cubic net (**pcu**) (Fig. S8†).

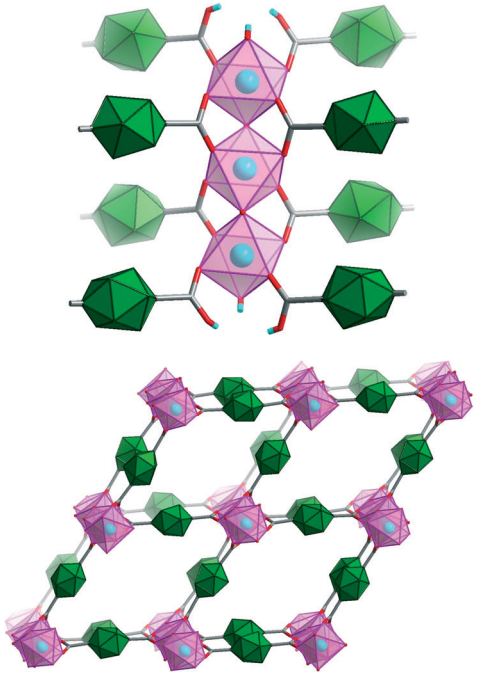


Fig. 2 [Co(DMF)L] (**2**) based on an infinite $\{Co_2\{\mu\text{-}O_{DMF}\}(RCOO)_4\}_\infty$ ribbon SBU (top), resulting in a structure which could be interpreted as a 'quasi' **pcu** net (bottom).

The robust framework is based on a ribbon-like coordination bonded backbone assuring dense pore walls and impossibility of interpenetration. The structural organization is practically the same as that in the paradigmatic MIL-53 flexible PCP, with the only principal difference being the nature of the short O_{DMF}-bridge: in the case of **2**, it belongs to a DMF molecule (Fig. S10†) and could in principle be removed; on the other hand, in MIL-53, it belongs to a bridging hydroxy group, which serves as a counteranion to the central atom of a higher charge and cannot be straightforwardly removed. Activation of **2** at 300 °C under vacuum yields the DMF-free (Fig. S22†) **2a**, which has an S_{BET} = 382 m^2 g^{-1} (N_2, 77 K) (Fig. 3). The experimentally determined surface area is

Table 1 Summary of selected data for compounds **1**–**3**

Compound[a]	Space group; node connectedness {node}, {point symbol} three letter code	Surface area of the degassed structure, experimental[b] (calculated)[c]/m^2 g^{-1}	Void volume part, experimental[d] (calculated)[e]/cm^3 cm^{-3}	Additional data: density after degassing/g cm^{-3}, HOA (zero coverage)/kJ mol^{-1}
$[Zn_4OL_3(DEF)_3]$, **1**	*Pna*2_1; 6-c $\{Zn_4O(RCOO)_6\}$, $\{4^8{\cdot}6^6{\cdot}8\}$ **rob**	896 (1945)	0.383 (0.532)	ρ_{calc} = 0.898 ~>4 × 4 Å aperture
[Co(DMF)L], **2**	*C*2/*c*; 'quasi' 6-c for $\{Co_2\{\mu\text{-}O_{DMF}\}(RCOO)_4\}_\infty$ equiv. to $\{4^{12}{\cdot}6^3\}$ **pcu**[f]	382 (679.6)	0.169 (0.358)	ρ_{calc} = 1.129, HOA(H_2) = 5.7 HOA(CO_2) = 22.8 ~5 × 5 Å aperture
$[Cu_2L_2(DMF)_2]$ ·2DMF, **3**	*I*4$_1$*md*; 4-c $\{Cu_2(RCOO)_4\}$, $\{4^2{\cdot}8^4\}$ **lvt**	–(3729)[g]	–(0.677)	ρ_{calc} = 0.699 ~5 × 6 Å aperture

[a] The solvent content was confirmed/established using TGA (ESI). [b] Experimental S_{BET} values (N_2, 77 K; P/P_0 = 0.01–0.12 interval). [c] The values are calculated[18] for a model, in which the coordinates of the atoms were taken from the SC XRD data, while the solvent molecules were excluded. Idealized hydrogen atoms were added for **3**. [d] Experimental total pore volume (cm^3 g^{-1}) at P/P_0 = 0.95 multiplied by density, given in the next column, based on crystallographic data for a structure with guest molecules removed. [e] Void volume as calculated by Platon.[24] [f] Probably non-attainable, which is associated with the flexibility of the framework. [g] A possible interpretation based on dissection of the infinite coordination bonded motif.

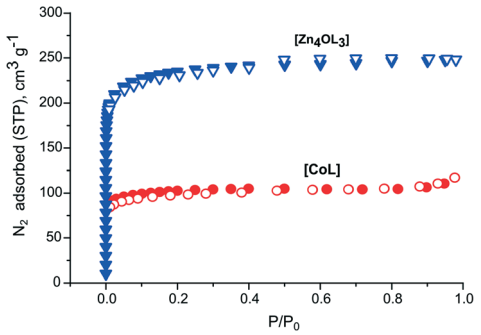


Fig. 3 N_2 adsorption isotherms (77 K) for **1a** (blue) and **2a** (red).

lower than the value calculated from the structural data (679.6 $m^2\ g^{-1}$).[18] Aside from possible partial structural collapse during activation caused by escape of DMF molecules, which are comparable in size and pore dimensions, flexibility, analogous to the one observed for MIL-53, could also be a factor contributing to the difference. The deep violet, almost black (*cf.* with the initial red colour), material is very intriguing, despite its relatively low surface area, as it should possess 'chelating' unsaturated metal centers (UMS),[23] which could fasten the substrate molecule simultaneously, providing enhanced binding. Indeed, the modest H_2 adsorption (82 $cm^3\ g^{-1}$ STP, 1 bar and 77 K) is characterized by the considerable zero-coverage isosteric heat of adsorption value of 5.4 kJ mol^{-1} (77–87 K), which is, however, still lower than expected for such a material. The CO_2 adsorption reaches 1.9 mmol g^{-1} at 1 bar and 0 °C, and the zero-coverage isosteric heat of adsorption is 23 kJ mol^{-1} (Table 1).

The structure of **2** is principally different compared to a known icosahedral carborane-based analog, $[Co_4(OH)_2L'_3(DMF)_2]$. The activated form of the latter is the most porous carboranedicarboxylate-only based PCP known to date (S_{BET} = 1080 $m^2\ g^{-1}$, H_2 uptake at 77 K is 181 $cm^3\ g^{-1}$) and, built upon isolated $\{Co_4(OH)_2(COO)_6\}$, it is the closest analog of an elusive MOF-5 type structure.[11a] Although its formal adsorption parameters are better than in the case of **2a**, mainly due to its higher specific surface area, no special prerequisites for specific adsorption or flexibility are present.

An even more intriguing example of dissimilarity between the 10- and 12-vertex carboranedicarboxylate PCPs was found by examination of their copper complexes. Both H_2L and H_2L' were used under a range of different conditions. In all cases except for one, greenish or greenish-blue lamellar solids were obtained and the lamellae had a distinctive square form. However, when a small amount of nitric acid was added to the DMF-based reaction mixture, blocks with good crystallinity were obtained, but only in the case of H_2L.

The observation of the square lamellae is in agreement with the anticipated simple layered structure with a $4^4{\cdot}6^2$ 'square' net (**sql**) topology, based on the $\{Cu_2(COO)_2\}$ 'paddlewheel' SBU. The formation of such a structure was confirmed for the 1,12-dicarboxy-*closo*-1,12-dicarbadodecaborane as a ligand (H_2L'), demonstrating the expected prevalence of that structural organization.[20] To our surprise, the only distinct phase with high crystallinity, synthesized under modified conditions, is the $[Cu_2L_2(DMF)_2]{\cdot}2DMF$, **3**. It has a 3D framework structure (Fig. 4) with a considerably large unit cell ($V \sim 11$ $kÅ^3$), while its topology represents a simple uninodal **lvt** net.

The realization of the **sql** topology is by a high margin the most probable for building blocks that could adopt a planar conformation, *e.g.* the terephthalate ligand, where planarity is favored by conjugation. Introduction of a single *ortho*-substituent in terephthalate effectively de-planarizes the ligand and this is a known approach[21] for rational synthesis of 3D **nbo** type structures with significant porosity, representing the second most probable structural organization. The realization of the **lvt** topology in **3** is unusual and demands special complex deflection from planarity, which is seemingly fulfilled because of the relatively low rotation barrier of the carboxylate groups. It is known that the carboxylate group of 1,12-*closo*-dicarbadodecaboranecarboxylate has a very low rotation barrier (<0.5 kJ mol^{-1}) compared to that of benzoate (~6 kJ mol^{-1}),[22] but exact information about the rotation barrier in 1,10-*closo*-carboranecarboxylate is far less available. According to our calculations, the rotation barrier for the latter (see the ESI†) is 2.48 kJ mol^{-1}, which is approx. an order of magnitude higher than the 0.22 kJ mol^{-1} value for the icosahedral analogue, but still significantly smaller than that of benzoate. The curious shape of the energy profile (Fig. S35†) demonstrates a broad plateau near 0° of the dihedral angle, which corresponds to an eclipsed position of the carboxylate plane and the C–B bond. Accordingly, the most probable interplanar angle between the carboxylate groups in L^{2-} is 45°, which is in accordance with the antiprismatic geometry of the cage. That deflection seems to be enough to induce

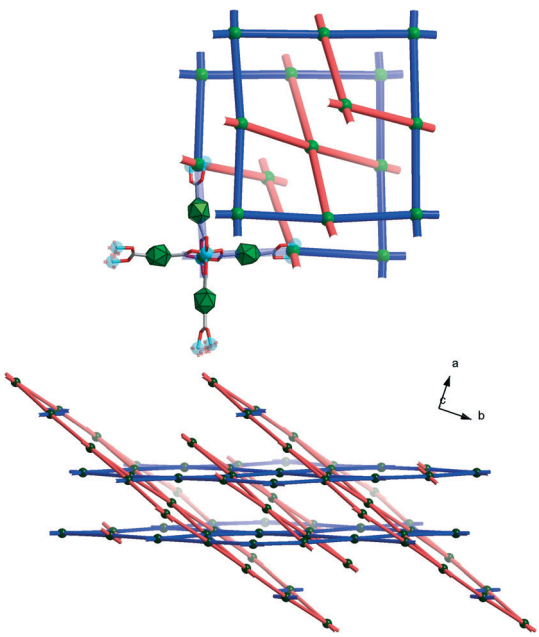


Fig. 4 A representative fragment of the $[Cu_2L_2(DMF)_2]{\cdot}2DMF$ (**3**) structure: an expansion of the paddlewheel motif sustaining the nodes of the **lvt** net (top) and the net itself (bottom). The colouration of the net illustrates its interpretation as a fusion of simpler (4,4) subnets.

the formation of a non-**sql** topology under certain conditions, but not an **nbo** one, for which an interplanar angle of 90° is optimal. For the 12-vertex analog there is practically no preferred orientation, so broad isomerism should be possible, but our attempts to synthesize any non-**sql** phases were unsuccessful, which might be explained by slightly more demanding steric requirements.

3 has a very open framework structure with a calculated porosity of ~3700 $m^2\ g^{-1}$ for the hypothetical solvent-free **3a**,[17] potentially exceeding even the value for the best linear spacer-based carborane-containing (however, mostly non-carborane) NU-135 PCP which is 2700 $m^2\ g^{-1}$ (2530 $m^2\ g^{-1}$ is the experimentally proven value).[13] Unfortunately, direct activation without solvent exchange is not possible for copper-based PCPs containing DMF due to reductive degradation; hence, milder post-exchange super critical drying[23] is to be implemented. It is expected that the experimental surface area will be smaller than the calculated value due to the evident predisposition of the framework to flexible behaviour, enhanced by the low rotation barrier of the carboxylate groups. On the other hand, the compound is an excellent prototype of a highly porous 'swivel'-flexible PCP.

In summary, some of the newly reported PCPs are among the most porous simple carboranedicarboxylate-based PCPs and demonstrate unexpected uniqueness not only in comparison with terephthalate, but even with known 12-vertex icosahedral carborane analogs, which allows to regard 10-vertex carboranes as a distinct PCP–ligand platform. The prospects of rich chemistry of the new building blocks are supported by the relatively low rotational barrier of the carboxylate groups attached to the carboranes, slightly favouring non-coplanar disposition of the building blocks and the decreased tendency towards the preferred orientation conditioned by π–π stacking. Investigation on scaled-up homologues, as well as in-depth investigation on the promising sorptive properties of new materials, is underway.

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